



Short communication

Performance of the “SiO”—carbon composite-negative electrodes for high-capacity lithium-ion batteries; prototype 14500 batteries

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H I G H L I G H T S

- ▶ The silicon-based negative electrodes can be used in practical lithium-ion batteries.
- ▶ The prototype 14500 batteries show 1 Ah of nominal capacity.
- ▶ The performance is superior to the conventional batteries based on graphite.
- ▶ The batteries show neither smoke nor fire for all the tests examined.

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Prototype 14500 batteries (14 mm dia. and 50 mm hgt.; AA size) consisted of the “SiO”—carbon composite-negative and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{LiCoO}_2$ (7/3 by weight)-positive electrodes were designed, fabricated and examined in voltage ranging from 2.5 to 4.2 V at -20 , -10 , 0 , and $+23$ °C. The batteries were stored and delivered 1 Ah at 200 mA and 0.96 Ah at 2 A, and the capacity remained after 300 cycles at 23 °C was 0.7 Ah. Abuse tests, such as overcharging to 12 V, nail penetration, and heating of fully charged batteries in an oven at 150 °C, were also carried out and shown that the batteries showed neither smoke nor fire for all the tests examined. The battery performance was compared to that of conventional batteries with graphite-negative electrodes in the same size and the characteristic features of the lithium-ion batteries with the SiO–carbon composite-negative electrodes were discussed from the experimental results.

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1. Introduction

During the past 10 years, we have been studying high-capacity negative-electrode materials [1–4] substituting for the graphite-negative electrodes in order to increase capacity and consequently the energy density of lithium-ion batteries. Among possible materials of the negative electrodes, we have selected silicon and improved its capacity fading due to the change in volume during charge and discharge. Initial trials on the silicon-negative electrodes, such as an application of thin-film of silicon to the negative electrodes, silicon–carbon composite, and porosity-controlled silicon–carbon composite to buffer the change in volume during charge and discharge, have not given good results [1–3]. We have learned a lot during our initial trials on silicon that nano-size silicon particles are inevitably necessary to improve the

capacity fading, leading to the “SiO”—carbon composite-negative electrodes [5,6].

“SiO” consists of nano-size silicon and amorphous silicon dioxide by an atomic ratio of one to one, and the “SiO”—carbon composite material is composed of 50 weight percents (wt%) “SiO”, 21 wt% graphite, 9 wt% carbon fiber, and 20 wt% carbon [5,6]. As shown in a previous paper [6], “SiO” consisting of nano-size silicon particles dispersed in amorphous SiO_2 is converted to lithium–silicon alloy particles, $\text{Li}_{3.75}\text{Si}$, surrounded by amorphous lithium silicon oxides, mainly Li_4SiO_4 , during the first charge of the negative electrode in lithium-ion batteries, and the lithium–silicon alloy particles surrounded by a lithium-ion conductor of amorphous lithium silicon oxides are rechargeable for subsequent cycles. Therefore, such an electrode is expected to be safe together with high capacity, because high-capacity lithium silicon alloys are covered with or coated by lithium silicon oxides. However, the characters associated with safety combined with battery performance cannot be evaluated unless the prototype batteries are fabricated and examined.

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In this paper, we report the performance of cylindrical 14500-prototype batteries consisting of the “SiO”–carbon composite-negative electrodes and lithium nickel manganese cobalt oxide (NMC)–lithium cobalt oxide (LCO)-positive electrodes and discuss the characteristic features of new high-capacity lithium-ion batteries in contrast to current lithium-ion batteries consisting of graphite-negative and layered transition metal oxide-positive electrodes.

2. Experimental

The “SiO”–carbon composite material used in this paper is the same as described previously [5]. The negative electrodes consist of 90 wt% “SiO”–carbon composite material, 2 wt% carbon black, and 8 wt% polyvinylidene difluoride (PVdF) on copper foil. The positive electrodes consist of 97.25 wt% positive-electrode material, 1.5 wt% carbon black, and 1.25 wt% PVdF on aluminum foil. The positive-electrode material selected is the mixture of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC) [7,8] and LiCoO_2 (LCO) by the weight ratio of 7 to 3. The cell hardware used to fabricate prototype batteries is cylindrical 14500 (14 mm dia. and 50 mm hgt.), which is known as AA size batteries. One-ampere-hour batteries are designed, fabricated, and examined in voltage ranging from 2.5 to 4.2 V. The electrolyte is 1 M LiPF_6 ethylene carbonate (EC)/diethyl carbonate (DEC) (3/7 by volume). Vinylene carbonate (VC) [9,10] and fluoroethylene carbonate (FEC) [11,12] are used as additives in the electrolyte in fabricating 14500 lithium-ion batteries. The other sets of experimental conditions are described in results and discussion section.

3. Results and discussion

3.1. Basic parameters used to design prototype 14500 batteries

In order to design 14500 lithium-ion batteries consisting of “SiO”–carbon composite-negative and NMC/LCO(7/3 by weight)-positive electrodes, we need basic data on the first charge capacity in mAh g^{-1} , the weight ratio of active material in wt%, the electrode density in g cm^{-3} , and the coating weight in mg cm^{-2} for both positive and negative electrodes. The thicknesses of Al-foil, Cu-foil, and separator are fixed when these materials are selected. Therefore, if the coating weight is determined, the weight of battery, the first Ah-efficiency, and the rechargeable capacity of a battery are calculated from the basic data. The coating weight is determined under such a condition that the current corresponding to 1C rate is 3.4 mA cm^{-2} in this case, in which C is the nominal capacity of the battery to be determined by the examinations while the rechargeable capacity expected at 1C rate is used substituting for the nominal capacity to calculate the coating weight. Table 1 summarizes basic parameters used to design 14500 lithium-ion batteries. The rechargeable capacity expected is 1080 mAh. The first Ah-efficiency of the battery is assumed to be 73% because the first Ah-efficiency of the negative electrode is 73% [5,6] and that of the positive electrode is very close to 100%.

3.2. Nominal capacity determined for the prototype 14500 batteries

Fig. 1 shows the discharge curves of the 14500-cylindrical prototype battery operated at 23 °C. The 14500 lithium-ion batteries consisting of LiCoO_2 and graphite are also shown in Fig. 1 for comparison. The nominal capacity is determined from the discharge capacity observed at the 5-h rate. The nominal capacity determined for the new 14500 lithium-ion batteries is 1000 mAh while that of the conventional batteries is 750 mAh, so that the currents delivered from the new battery (II) is 1.33 times larger than those from battery (I) when the C-rate is applied to examine

Table 1

Basic parameters used to design 14500 lithium-ion batteries consisting of the “SiO”–carbon composite-negative and NMC/LCO(7/3 by weight)-positive electrodes. The rechargeable capacity of the battery is expected to be 1080 mAh.

Item	Unit	Value determined
Positive electrode		
The first charge capacity	mAh g^{-1}	168
Active material in the mix	wt%	97.25
Density of the electrode mix	g cm^{-3}	3.40
Coating weight ^a	mg cm^{-2}	29.5
Thickness of aluminum foil	μm	15
Negative electrode		
The first charge capacity	mAh g^{-1}	1200
Active material in the mix	wt%	90
Density of the electrode mix	g cm^{-3}	1.30
Coating weight ^a	mg cm^{-2}	4.46
Thickness of copper foil	μm	8
Thickness of separator	μm	18
First Ah-efficiency of the battery assumed	%	73
Current density corresponding to 1C-rate	mA cm^{-2}	3.42
Rechargeable capacity designed	Ah	1.08
Battery weight calculated and measured	g	21
Battery volume calculated	cm^3	7.3

^a Coating weight was determined under such a condition that the current corresponding to 1C rate is 3.4 mA cm^{-2} .

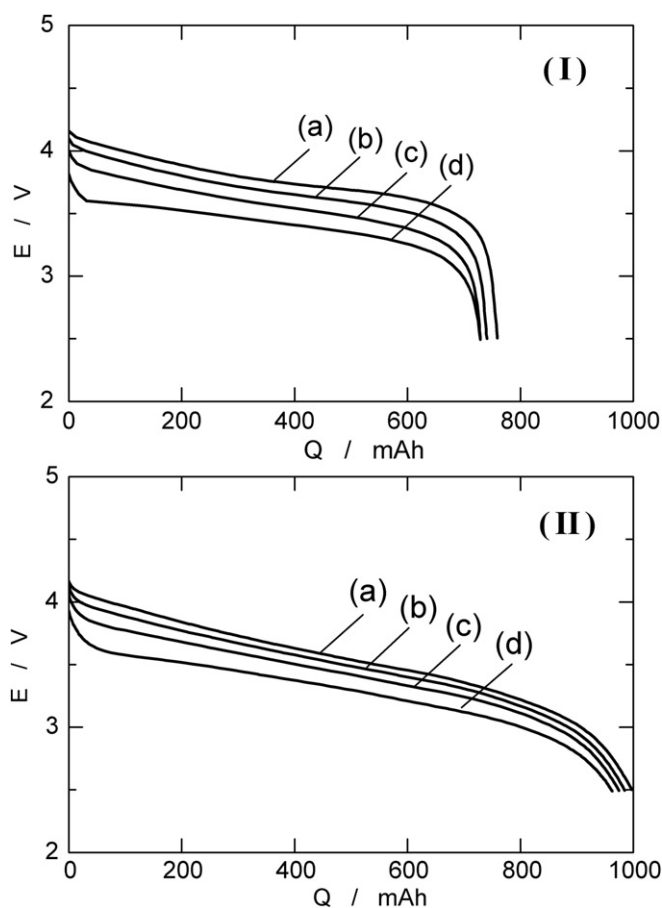


Fig. 1. Discharge curves of the 14500 lithium-ion batteries operated at (a) 1/5, (b) 1/2, (c) 1, and (d) 2C rates at 23 °C. The nominal capacity of battery (I) consisting of LiCoO_2 and graphite is 750 mAh and that of battery (II) consisting of the “SiO”–carbon composite-negative and NMC/LCO(7/3 by weight)-positive electrodes is 1000 mAh.

the batteries. In Fig. 1, the discharge currents are adjusted to be (a) 1/5, (b) 1/2, (c) 1.0, and (d) 2.0 C-rate in mA based on the nominal capacity in mAh for both (I) and (II). In other words, the currents applied to the new 14500 battery (II) are specifically (a) 200, (b) 500, (c) 1000, and (d) 2000 mA. The new batteries are charged at constant current of 500 mA (1/2C-rate) until the terminal voltage reaches 4.2 V and then kept at 4.2 V until the total charging time reaches 3 h, i.e., constant-current and constant-voltage charge for 3 h, abbreviated CCCV(1/2C, 4.2 V, 3 h) charge hereafter. After charge, the batteries are discharged at 200(1/5C), 500(1/2C), 1000(1C), or 2000(2C) mA until the terminal voltage reaches 2.5 V. As clearly seen in Fig. 1, the operating voltage of the new battery draws slopping curves in voltage ranging from 4.2 to 2.5 V. The average operating voltage is approximately 3.5 V, which is 0.2 V lower than that of lithium-ion batteries with the graphite-negative electrodes. This is mainly due to the difference in operating voltage of the negative electrodes. The average operating voltage of “SiO”-carbon composite electrode is ca. 0.2 V higher than that of graphite electrode when they are examined in lithium non-aqueous cells [5,13].

The ratio of discharge capacities observed at 2C-rate to those at 1/5C rate is usually used to evaluate the rate capability of the batteries. The value calculated for the new batteries is 97% while it is 96% for the conventional 14500 batteries, indicating that the trial batteries show the same rate capability as the conventional batteries. In fact, the new batteries deliver 1.33 times higher currents than the conventional batteries because of its nominal capacity. A characteristic feature of the new 14500 batteries with the “SiO”-carbon composite-negative electrode is high capacity as has been expected. The conventional 14500 batteries available in market are 750–800 mAh of nominal capacity. Therefore, one may say that the new 14500 lithium-ion batteries show 1.2–1.33 times larger capacity than the conventional batteries. When one compares the nominal capacity of the new 14500 batteries with that reported in 1994 [14], the nominal capacity increases more than 2 times, i.e., 450 mAh in 1994 versus 1000 mAh in this paper, mainly due to the innovation of the negative-electrode materials.

3.3. The performance of prototype 14500 batteries

The discharge curves observed at -20 , -10 , 0 , and $+23$ °C are shown in Fig. 2. The discharge current applied to the batteries is 1C rate for both batteries, i.e., 750 mA for a conventional battery (I) and 10000 mA for the prototype battery (II). As seen in Fig. 2, the low-temperature performance of the prototype battery is superior to that of a conventional battery. If we define the values to evaluate the low-temperature performance of batteries as the ratio of the discharge capacity at -20 °C to that at $+23$ °C at 1C rate, the new prototype batteries score 32% in contrast to 3% for conventional batteries.

Fig. 3 shows the rechargeable capacity as a function of cycle number for both 14500 batteries. The charge and discharge cycle consists of the CCCV (1/2C, 4.2 V, 3 h) charge and the constant-current discharge at 1C rate to 2.5 V at 23 °C. The currents are specifically 375 mA on charge and 750 mA on discharge for the conventional batteries (I) while 500 mA on charge and 1000 mA on discharge for the new batteries (II). As seen in Fig. 3, the capacity fading for the prototype 14500 batteries is faster than that for conventional batteries. The discharge capacities of the new batteries are larger than those of conventional batteries in cycle number up to 250 cycles. In other words, the Ah-capacity stored in and delivered from the new 14500 batteries after 250 cycles is the same as that of conventional lithium-ion batteries. Although some of improvements must be done in terms of cycle performance, the capacity fading due to the volume change of silicon during charge

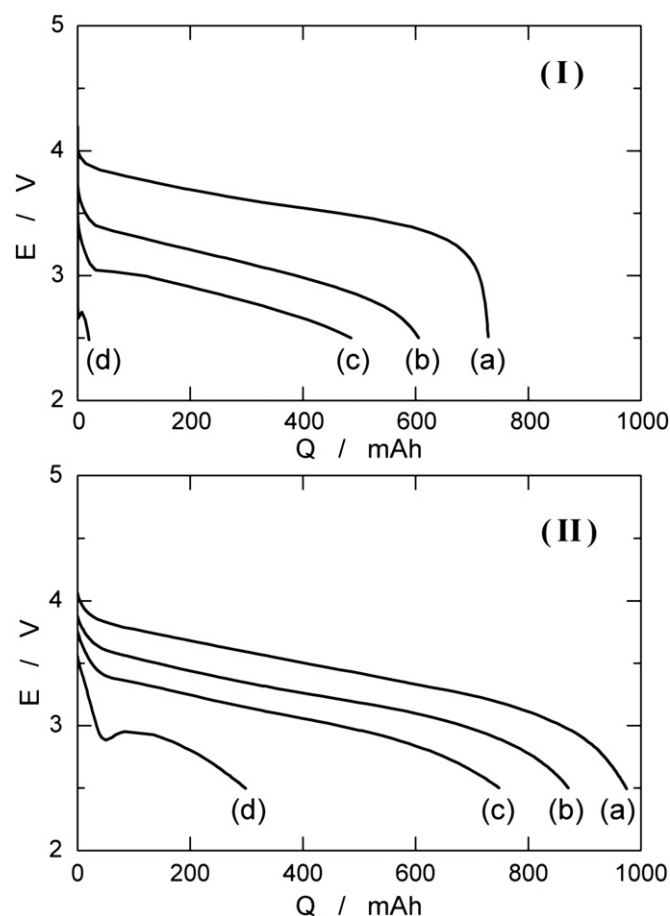


Fig. 2. Discharge curves of the 14500 lithium-ion batteries operated at 1C rate at (a) $+23$, (b) 0 , (c) -10 , and (d) -20 °C. Battery (I) consists of LiCoO_2 and graphite. Battery (II) consists of the “SiO”-carbon composite-negative and NMC/LCO(7/3 by weight)-positive electrodes. Nominal capacities are 750 mAh for battery (I) and 1000 mAh for battery (II).

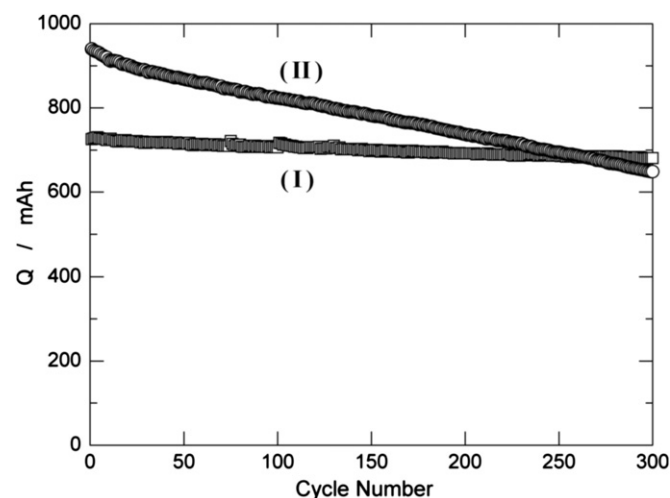


Fig. 3. Rechargeable capacities as a function of cycle number for the 14500 lithium-ion batteries operated at 23 °C. Battery (I) having the nominal capacity of 750 mAh consists of LiCoO_2 and graphite. Battery (II) having the nominal capacity of 1000 mAh consists of the “SiO”-carbon composite-negative and NMC/LCO(7/3 by weight)-positive electrodes. After the CCCV (1/2C, 4.2 V, 3 h) charge, the batteries are discharged at 1C rate to 2.5 V, and this cycle is continuously repeated for 300 times.

and discharge is remarkably improved by applying the “SiO”–carbon composite material to the negative electrode in lithium-ion batteries, which are specifically due to the combined effect of nano-size lithium silicon alloys covered with lithium silicon oxides and the composite structure of carbon and “SiO” to buffer the change in volume of “SiO” particles [6].

Fig. 4 shows an example of the storage tests at 60 °C for 20 days. After the CCCV (1/2C, 4.2 V, 3 h) charge, the batteries were stored at 60 °C for 20 days, cooled to 23 °C, and then the battery was discharged at 1C rate. The residual capacity observed after the high-temperature storage at 60 °C for 20 days was 670 mAh. Capacity of ca. 300 mAh was lost during the storage. However, some of the capacities are recovered when the batteries are charged and discharged [15]. After the CCCV (1/2C, 4.2 V, 3 h) charge, the battery was discharged at 1C rate to 2.5 V as shown in Fig. 4. Although the rechargeable capacity fades ca. 15%, a fatal damage of the prototype batteries cannot be seen even after the storage of fully charged batteries at 60 °C for 20 days.

3.4. Safety inspection of the new 14500 batteries

As described above, the new 14500 batteries with the “SiO”–carbon composite-negative electrodes are superior to the conventional batteries with the graphite-negative electrodes in terms of nominal capacity, volumetric and gravimetric energy densities, and low-temperature performance. The lithium-ion batteries have usually been furnished with a positive temperature coefficient (PTC) thermistor in addition to a circuit interrupt device (CID) as safety devices in order to secure against every kind of battery abuse. The history of lithium-ion batteries tells us that safety inspection is more important item than others associated with battery performance, such as high-rate capability, cycle life, self-discharge, etc. In order to examine what happens when the new 14500 batteries are abused, a series of safety inspection is carried out. A safety device installed in the new 14500 batteries is only CID. The PTC thermistor is not applied to the new batteries.

Fig. 5 shows an example of the nail penetration tests for the fully charged 14500 batteries. After CCCV (1/2C, 4.2 V, 3 h) charge, a nail 3.0 mm in diameter is penetrated at the middle of height of a 14500 battery in a radial direction at a penetration rate of 5 mm s^{−1} at 23 °C and the surface temperature of the battery is recorded. As seen in Fig. 5, the temperature increases almost linearly for 1 min

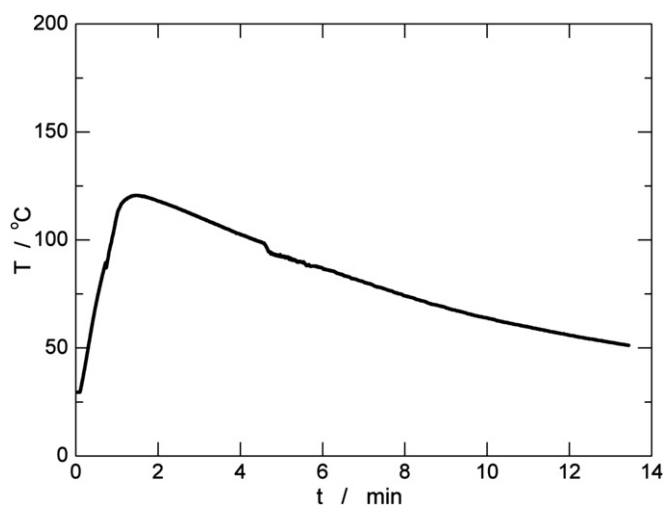


Fig. 5. Temperature on the battery surface as a function of time for the nail penetration test of the 14500 lithium-ion battery consisting of the “SiO”–carbon composite-negative and NMC/LCO(7/3 by weight)-positive electrodes. After the CCCV (1/2C, 4.2 V, 3 h) charge, a nail 3.0 mm in diameter is penetrated at a speed of 5 mm s^{−1}.

and then decreases. The maximum temperature observed is 120 °C in this case. During the nail penetration test, smoke and fire are not observed.

An example of the results on heating the 14500 batteries in an oven is shown in Fig. 6. The fully charged battery is heated from 23 to 150 °C in an oven at a heating rate of 5 °C min^{−1} with monitoring both temperatures in the oven and on the surface of the battery [16]. To avoid overheating above 150 °C, the heating rate is slowed down when the oven temperature approaches 150 °C. As clearly seen in Fig. 6, the battery is once heated up above 150 °C drawing two humps, and the surface temperature monotonously decreases and approaches the oven temperature of 150 °C, indicating no thermal runaway. During the heating tests in an oven, neither fire nor smoke is observed.

Fig. 7 shows an example of overcharge tests to 12 V. After the CCCV (1/2C, 4.2 V, 3 h) charge, the battery is further charged at 1C rate, specifically 1000 mA, to 12 V with monitoring the terminal

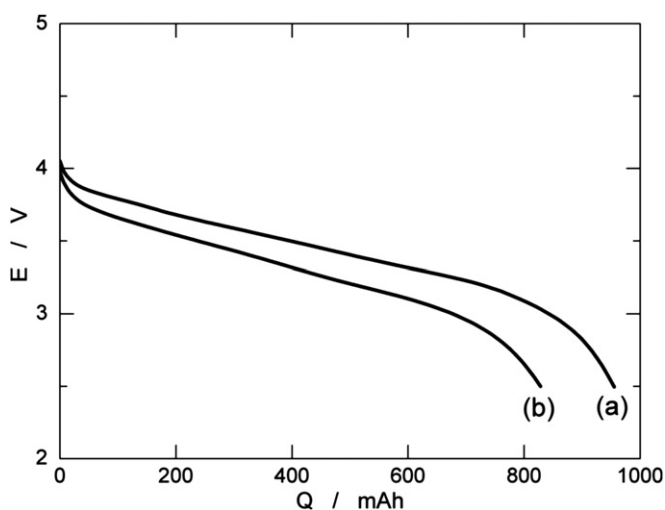


Fig. 4. Discharge curves of the 14500 lithium-ion battery with the “SiO”–carbon composite-negative electrode (a) before and (b) after the storage at 60 °C for 20 days. The batteries are discharged at 1C rate at 23 °C after the CCCV (1/2C, 4.2 V, 3 h) charge.

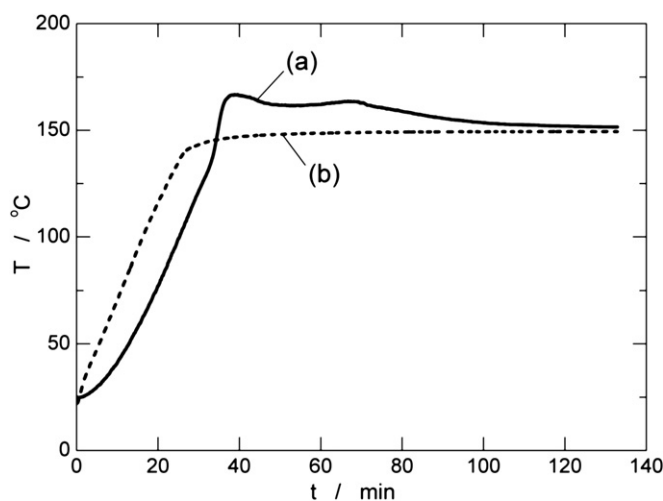


Fig. 6. Heating test of the 14500 lithium-ion battery consisting of the “SiO”–carbon composite-negative and NMC/LCO(7/3 by weight)-positive electrodes in an oven. After the CCCV (1/2C, 4.2 V, 3 h) charge, the battery is heated at a heating rate of 5 °C min^{−1} in an oven. Both temperatures (a) on the battery surface and (b) in an oven are monitored.

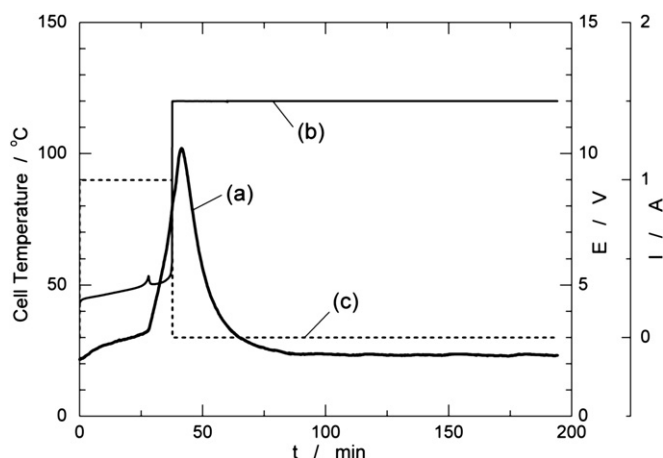


Fig. 7. Overcharge test of the 14500 lithium-ion battery consisting of the “SiO”–carbon composite-negative and NMC/LCO(7/3 by weight)-positive electrodes with monitoring (a) temperature on the battery surface, (b) the terminal voltage, and (c) current.

Table 2

Performance of the new 14500 lithium-ion batteries consisting of the “SiO”–carbon composite-negative and NMC/LCO(7/3 by weight)-positive electrodes.

Nominal capacity determined at 1/5C rate	Ah	1.00
Gravimetric energy density	Wh kg ⁻¹	180
Volumetric energy density	Wh dm ⁻³	510
Rate capability; the ratio of discharge capacities at 2C to 1/5C rate	%	96
Low-temperature performance; the ratio of the discharge capacity at 1C rate at –10 °C to that at +20 °C	%	80
Low-temperature performance; the ratio of the discharge capacity at 1C rate at –20 °C to that at +20 °C	%	32
High-temperature storage; capacity retention after the storage at 60 °C for 20 days	%	86
Cycle performance; capacity retention after 300 cycles at 23 °C	%	70
(Safety inspection)	(Outlook)	(Note)
Overcharge at 1C rate to 12 V	Passed	No fire No smoke
Nail penetration of fully charged battery	Passed	No fire No smoke
Heating the fully charged battery at 150 °C for 2 h	Passed	No fire No smoke

voltage, current, and surface temperature of the battery [17]. As seen in Fig. 7, the operating voltage increases up to 5.2 V with increasing temperature. At a protuberant signal in the voltage versus time curve, the cell temperature starts to increase rapidly, suggesting that the battery is internally short-circuited at this point. As the temperature increases, the internal pressure increases and then the CID is tripped. Consequently, the current stops and simultaneously the terminal voltage increases to 12 V. Although the battery temperature increases even after the CID works, it does not go infinity. The temperature once increases and then decreases, drawing a spike whose maximum temperature is about 100 °C. As clearly seen in Fig. 7, the batteries can be designed to be safe even for the overcharging of batteries by applying the “SiO”–carbon

composite material to the negative electrodes in lithium-ion batteries.

4. Summary

In this paper, we have reported the performance of prototype 14500 batteries consisting of the “SiO”–carbon composite-negative and NMC/LCO(7/3 by weight)-positive electrodes. The performance of prototype 14500 batteries examined is summarized in Table 2. The new batteries have more character than the conventional batteries in terms of high capacity, low-temperature discharge performance, and safety. The high-capacity lithium-ion batteries can be used for mobile electronic devices, such as digital still cameras, digital video cameras, etc. The “SiO”–carbon composite material developed is in a powered form, so that the processing method to make the negative electrodes is the same as that of graphite. The design flexibility makes it possible to apply new negative electrodes to prismatic batteries and others in addition to cylindrical batteries. The batteries using “nano-silicon technology” have already been commercialized since the second half of 2010.

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